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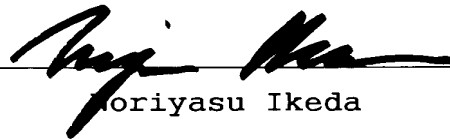
My name and post office address are as stated below;

That I am knowledgeable in the Japanese language in which the below identified Japanese application was filed, and that I believe the English translation of the Japanese application No. 91963/2000 is a true and complete translation of the above identified Japanese application as filed.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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the following application as filed with this Office.

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[Name of Document]                      Specification

[Title of the Invention]    METHOD FOR MANUFACTURING NITRIDE-BASED SEMICONDUCTOR LAYER

[Scope of Claim for a Patent]

[Claim 1]    A method for manufacturing a nitride-based semiconductor layer, characterized in that a heterosubstrate is removed from a nitride-based semiconductor layer grown on the heterosubstrate by using an etching solution to dissolve a substrate material.

[Claim 2]    The method for manufacturing a nitride-based semiconductor layer according to claim 1, characterized in that the heterosubstrate is dissolved after a protective film is formed on a surface of the nitride-based semiconductor layer.

[Claim 3]    The method for manufacturing a nitride-based semiconductor layer according to claim 1 or 2, characterized in that the nitride-based semiconductor layer is a nitride-based semiconductor thick film.

[Claim 4]    The method for manufacturing a nitride-based semiconductor layer according to claim 1 or 2, characterized in that the nitride-based semiconductor layer is a nitride-based semiconductor element structure.

[Claim 5]    The method for manufacturing a nitride-based semiconductor layer according to claim 3, characterized in that a nitride-based semiconductor element structure is

made on the nitride-based semiconductor layer after the substrate is removed.

[Claim 6] The method for manufacturing a nitride-based semiconductor layer according to claim 4 or 5, characterized in that the protective film also serves as an electrode of a nitride-based semiconductor element.

[Claim 7] The method for manufacturing a nitride-based semiconductor layer according to one of claims 1 to 6, characterized in that the heterosubstrate is a sapphire substrate, and the etching solution is a mixed liquid of phosphoric acid and sulfuric acid, or a mixed liquid containing the same.

[Claim 8] The method for manufacturing a nitride-based semiconductor layer according to one of claims 1 to 7, characterized in that the protective film is made of one selected from gold (Au), platinum (Pt), titanium (Ti)-gold (Au), palladium (Pd)-gold (Au), nickel (Ni)-gold (Au), Ti-platinum (Pd)-Au, AuZn, and AuGe.

[Claim 9] The method for manufacturing a nitride-based semiconductor layer according to one of claims 1 to 8, characterized in that the nitride-based semiconductor layer contains one of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ) and  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ).

[Claim 10] The method for manufacturing a nitride-based semiconductor layer according to one of claims 1 to 9, characterized in that the nitride-based semiconductor layer contains at least two materials of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ),  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ), and  $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$  ( $0 \leq x+y \leq 1$ ).

[Claim 11] The method for manufacturing a nitride-based semiconductor layer according to claim 7, characterized in that the removal of the sapphire substrate is carried out at an etching solution temperature of 300°C or higher.

[Claim 12] The method for manufacturing a nitride-based semiconductor layer according to one of claims 4 to 6, characterized in that the nitride-based semiconductor element structure is a semiconductor laser, a light emitting diode, or a field effect transistor.

[Claim 13] The method for manufacturing a nitride-based semiconductor layer according to one of claims 1 to 6, characterized in that a backside of the substrate side of the nitride-based semiconductor layer is polished to be flat after the substrate is removed.

[Detailed Description of the Invention]

[0001]

[Technical Field Pertinent to the Invention]

The present invention relates to a method for manufacturing a nitride-based semiconductor layer, and more particularly to a method for manufacturing a nitride-based semiconductor layer, which suppresses an influence on the nitride-based semiconductor layer when a substrate is removed from the nitride-based semiconductor layer epitaxially grown on a heterosubstrate.

[0002]

[Prior Art]

A nitride-based semiconductor, e.g., gallium nitride

(GaN), has a large forbidden bandwidth of 3.4 eV and is of a direct transition type, and thus it is used as a material for a blue light emitting element. Since a structure of a light emitting device is made by epitaxial growth, preferably, a bulk crystal similar in substance to an epitaxial layer to be grown is used as a substrate material. However, in the case of the crystal of GaN or the like, it is very difficult to form a bulk crystal because of high dissociation pressure of nitrogen, and it is difficult to make an element structure by carrying out epitaxial growth on the GaN single crystal substrate.

[0003]

Thus, a structure of a light emitting element is made by epitaxially growing a nitride-based semiconductor layer on a heterosubstrate which is different in physical or scientific properties such as a lattice constant and a thermal expansion coefficient from a nitride-based semiconductor, e.g., sapphire ( $\text{Al}_2\text{O}_3$ ), silicon (Si), silicon carbide (SiC), or zinc oxide (ZnO).

[0004]

Fig. 6 is a schematic view of a conventional nitride-based semiconductor laser structure section (S. Nakamura., Jan. J. Appl. 35,L74 (1996)). In Fig. 6, a nitride-based semiconductor laser structure is made by using metalorganic chemical vapor phase epitaxy (MOVPE). An undoped gallium nitride (GaN) buffer layer 52 is formed to a thickness of 30 nm on a sapphire substrate 51 in which a



(0001) surface is a front face. Then, layers are sequentially formed, i.e., an n type GaN contact layer 53 of a thickness  $3\text{ }\mu\text{m}$  to which silicon (Si) is added, an n type  $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$  54 of a thickness  $0.1\text{ }\mu\text{m}$  to which Si is added, an n type  $\text{Al}_{0.15}\text{Ga}_{0.85}\text{N}$  clad layer 55 of a thickness  $0.4\text{ }\mu\text{m}$  to which Si is added, an n type GaN optical guide layer 56 of a thickness  $0.1\text{ }\mu\text{m}$  to which Si is added, a multi-quantum well structure active layer 57 of 26 cycles which is constituted of an undoped  $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$  quantum well layer of a thickness 2.5 nm and an undoped  $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$  barrier layer of a thickness 5 nm, a p type  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$  layer 58 of a thickness 20 nm to which magnesium (Mg) is added, a p type GaN optical guide layer 59 of a thickness  $0.1\text{ }\mu\text{m}$  to which Mg is added, a p type  $\text{Al}_{0.15}\text{Ga}_{0.8}\text{N}$  clad layer 60 of a thickness  $0.4\text{ }\mu\text{m}$  to which Mg is added, and a p type GaN contact layer 61 of a thickness  $0.5\text{ }\mu\text{m}$  to which Mg is added. Lastly, a p type electrode 62 made of nickel (Ni)-gold (Au) is formed on the p type GaN contact layer 61, and an n type electrode 63 made of titanium (Ti)-aluminum (Al) is formed on the n type GaN contact layer 53.

[0005]

Ordinarily, a resonator mirror surface of a semiconductor laser is formed by using similarity of cleavage planes between the substrate and the laser element structure. However, if a nitride-based semiconductor laser is manufactured on a sapphire substrate which is one of the heterosubstrates, an angle between a (1-100) surface (M surface) which becomes a cleavage plane of an epitaxially

grown layer and an M surface which is a cleavage plane of the sapphire substrate is  $30^\circ$ , which makes it very difficult to form a resonator mirror surface by the cleavage plane of the sapphire substrate. Thus, the formation of the resonator mirror surface of the nitride-based semiconductor laser on the heterosubstrate must be carried out by reactive ion etching. In the case of the formation of the resonator mirror surface by the reactive ion etching, it is difficult to obtain a very smooth resonator surface.

[0006]

In the semiconductor laser element, contact electrodes are formed on a grown layer surface and a substrate backside. However, in the case of the nitride-based semiconductor laser element formed on a substrate such as a sapphire substrate which has no conducting properties, a contact electrode cannot be formed on the substrate backside and, as in the case of the formation of the resonator mirror surface, removal is carried out even on the contact layer of the substrate side by reactive ion etching to form a contact layer.

[0007]

[Problem to be Solved by the Invention]

A contact electrode can be formed on the nitride-based semiconductor layer of the backside by carrying out polishing to remove the heterosubstrate. To sufficiently endure the process or the polishing step, however, it is necessary to grow a thick nitride-based semiconductor layer

(e.g., GaN) of about 50  $\mu\text{m}$  or higher. However, thermal expansion coefficients are  $5.59 \times 10^{-6}/\text{K}$  of GaN and  $7.5 \times 10^{-6}/\text{K}$  of sapphire (thermal expansion coefficients in a c axis (longitudinal) direction of an upper side and an a axis (horizontal) direction of a lower side), which are greatly different from each other. Consequently, convex bowing occurs if the grown GaN layer is reduced to a normal temperature. The same holds true when the nitride-based semiconductor element structure is grown. It is difficult to uniformly polish the bowed sapphire substrate and, when the sapphire substrate becomes thin during polishing, a spherical ratio of the convex bowing is changed to cause cracks in the grown nitride-based semiconductor layer or element structure.

[0008]

An object of the present invention is to provide a method which suppresses an influence on an epitaxially grown layer to remove a substrate when a heterosubstrate is removed from a nitride-based semiconductor layer or a nitride-based semiconductor element structure grown on the heterosubstrate. Another object is to obtain a nitride-based semiconductor substrate or a nitride-based semiconductor element of high productivity and a large area by using a method for removing a heterosubstrate which reduces an influence on an epitaxially grown layer.

[0009]

[Means for Solving Problem]

According to the present invention, a method for

manufacturing a nitride-based semiconductor layer is characterized in that a heterosubstrate is removed from a nitride-based semiconductor layer grown on the heterosubstrate by using an etching solution to dissolve a substrate material. The method is characterized in that the heterosubstrate is dissolved after a protective film is formed on a surface of the nitride-based semiconductor layer.

[0010]

The nitride-based semiconductor layer may be a nitride-based semiconductor thick film, or the nitride-based semiconductor layer may be a nitride-based semiconductor element structure. Additionally, a nitride-based semiconductor element structure may be made on the nitride-based semiconductor layer after the substrate is removed.

[0011]

The method is characterized in that the heterosubstrate is a sapphire substrate, and the etching solution is a mixed liquid of phosphoric acid and sulfuric acid, or a mixed liquid containing the same. Preferably, the removal of the sapphire substrate is carried out at an etching solution temperature of 300°C or higher in consideration of productivity.

[0012]

The protective film may also serve as an electrode of a nitride-based semiconductor element. The protective film is made of one selected from gold (Au), platinum (Pt), titanium (Ti)-gold (Au), palladium (Pd)-gold (Au), nickel

(Ni)-gold (Au), Ti-platinum (Pd)-Au, AuZn, and AuGe.

[0013]

The method is characterized in that the nitride-based semiconductor layer contains one of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ) and  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ). Alternatively, the method is characterized in that the nitride-based semiconductor layer contains at least two materials of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ),  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ), and  $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$  ( $0 \leq x+y \leq 1$ ).

[0014]

The nitride-based semiconductor element structure is one of a semiconductor laser, a light emitting diode, and a field effect transistor. A backside of the substrate side of the nitride-based semiconductor layer may be polished to be flat after the substrate is removed.

[0015]

[Mode for Carrying Out the Invention]

In the mode for carrying out the invention, by taking an example of a sapphire substrate which is one of grown substrates of a nitride-based semiconductor, description will be made of a method for removing a substrate from a nitride-based semiconductor layer epitaxially grown on a heterosubstrate by using an etching solution to dissolve a substrate material.

[0016]

Regarding the etching solution to dissolve the sapphire, there is a report on etching of the sapphire by increasing a temperature of a mixed liquid of phosphoric acid

(86%) and sulfuric acid (95%) (L. A. Mara Sin a et al., Crystal Res. & Technol. 17 1982 3 365 to 371). This is a report about an etching rate of the sapphire by the mixed liquid, but nothing has been reported about an influence on other materials, especially an influence on a nitride-based semiconductor layer (e.g., GaN) epitaxially grown on the sapphire substrate.

[0017]

The inventors made an experiment on dissolution of the sapphire substrate by paying attention to the etching solution to dissolve the sapphire. As in the case of the aforementioned report, a mixed liquid of phosphoric acid and sulfuric acid was used for the etching solution of the sapphire substrate, and an etching temperature was set to 300°C. As a result, it was discovered that an etching rate was low, i.e., about 10  $\mu\text{m}/\text{hour}$ , at the temperature of 300°C, and a long time of 120 hours was necessary in order to etch and remove the sapphire substrate of a thickness 300  $\mu\text{m}$ . Further, an experiment was made for GaN under similar conditions in order to investigate an influence of the mixed liquid on the nitride-based semiconductor. It was discovered that when the temperature of the mixed liquid was increased to 300°C or higher, the GaN was etched at an etching rate of 10  $\mu\text{m}$  or higher/hour.

[0018]

Subsequently, in order to investigate a relation between a ratio of phosphoric acid/sulfuric acid in the mixed

liquid and an etching rate ( $\mu\text{m}/\text{hour}$ ), an experiment was made on etching of the sapphire substrate by changing a ratio of a sulfuric acid/phosphoric acid in the mixed liquid at a constant temperature. According to the experiment, etching was carried out for the sapphire substrate in the mixed liquid of phosphoric acid and sulfuric acid for a given length of time, and an etching rate ( $\mu\text{m}/\text{hour}$ ) was obtained by calculating a difference in thickness between the substrates before and after etching. A temperature was kept constant at  $335^{\circ}\text{C}$ , and a ratio of phosphoric acid and sulfuric acid in the etching solution was changed to 1:0.5 to 3. Additionally, to limit a reduction in the amount caused by evaporation of the phosphoric acid and the sulfuric acid, and a change in concentration, a beaker equipped with a circulator was used, and the etching was carried out after sufficiently evaporating moisture contained in the mixed liquid of the phosphoric acid and the sulfuric acid.

[0019]

Fig. 2 shows a relation between a ratio of sulfuric acid/phosphoric acid in the mixed liquid and an etching rate for the sapphire. As shown in Fig. 2, the sapphire substrate was etched by about  $80 \mu\text{m}/\text{hour}$  by setting a ratio of sulfuric acid/phosphoric acid to 0: 1 to 3 at a solution temperature of  $335^{\circ}\text{C}$ .

[0020]

By the experiment, it was discovered that it was possible to stably control a set temperature of the mixed

liquid by removing the moisture contained in the mixed liquid, and to carry out etching at a constant rate because the etching time and the etching amount of the sapphire were proportional to each other.

[0021]

Then, an experiment was made on changes in etching rates of the nitride-based semiconductor and the sapphire when the temperature of the mixed liquid of the phosphoric acid and the sulfuric acid was changed. A ratio of the sulfuric acid/phosphoric acid in the mixed liquid was set to 1:2, and the temperature of the mixed liquid was changed between 240°C and 360°C. As a sample, a sapphire substrate on which GaN was epitaxially grown was used.

[0022]

Fig. 3 shows a relation between a temperature of the mixed liquid and an etching rate of GaN or sapphire. As apparent from Fig. 3, the etching rates of the sapphire and the GaN were increased in proportion to the temperature of the mixed liquid of the phosphoric acid and the sulfuric acid. Additionally, it was discovered that since the etching rate of the GaN was lower compared with that of the sapphire, it was possible to remove by etching only the sapphire substrate from the sapphire substrate having a nitride-based semiconductor layer or a nitride-based semiconductor element structure by using a difference between the etching rates of both.

[0023]



The mixed solution dissolves not only the sapphire substrate but also the GaN layer. Thus, a GaN surface was observed to find concavoconvex roughness on the surface of the GaN layer. Thus, in order to prevent surface roughness of the nitride-based semiconductor layer, a protective film is formed on the surface of the nitride-based semiconductor, and the substrate is dissolved. The formation of the protective film on the surface enables enlargement of the etching rate difference between the nitride-based semiconductor and the sapphire without any direct influence on the nitride-based semiconductor even when the temperature of the mixed liquid is raised to increase the etching rate of the sapphire substrate. Thus, it is possible to remove the sapphire substrate within a short time.

[0024]

Preferably, the protective film formed on the surface of the nitride-based semiconductor has etching resistance with respect to the mixed liquid and, further, a material/constitution which has only a small influence on the nitride-based semiconductor is preferred in the step of forming or removing the protective film.

[0025]

<First Embodiment> A first embodiment of the present invention will be described by referring to Figs. 1(a) to 1(d). According to the first embodiment, from a structure in which a nitride-based semiconductor thick film is grown on the sapphire substrate, the sapphire substrate is removed by

an etching solution to form a nitride-based semiconductor thick film substrate.

[0026]

First, a GaN buffer layer 12 is formed to a thickness of about 1  $\mu\text{m}$  on a sapphire substrate 11 of a (0001) surface of a thickness 300  $\mu\text{m}$  by using metalorganic chemical vapor phase epitaxy (MOVPE). Then, an  $\text{SiO}_2$  film is formed on the GaN buffer layer 12, and separated into a mask 13 and a growth region 14 by a photolithography method and wet etching. The mask ( $\text{SiO}_2$  film) 13 and the growth region 14 are formed in stripe shapes of 4  $\mu\text{m}$  and 3  $\mu\text{m}$  in width, and a stripe direction is inclined by  $10^\circ$  from a direction of [11-20]. Subsequently, vapor phase epitaxy (VPE) of a chloride transport method which uses hydrogen chloride ( $\text{HCl}$ /gallium ( $\text{Ga}$ ), ammonia ( $\text{NH}_3$ ), and hydrogen ( $\text{H}_2$ ), GaN growth is carried out at a growth temperature of  $1000^\circ\text{C}$ , an  $\text{HCl}$  amount 1000cc/min. supplied to the Ga, and  $\text{NH}_3$  gas 1000cc/min. to bury the growth region 14 and the mask 13. By growth of 180 min., a flat-surface and highly crystalline GaN film 15 of a thickness 250  $\mu\text{m}$  is obtained on the sapphire substrate (Fig. 1(a)).

Subsequently, an  $\text{SiO}_2$  film 16 is formed to a thickness of 300 nm on the surface of the GaN film 15, and titanium (Ti) and gold (Au) are deposited to 50 nm and 0.4  $\mu\text{m}$  respectively in thickness to form a protective film 17 (Fig. 1(b)). After the formation of the protective film 17, 10-minute heat treatment is carried out in an hydrogen gas

atmosphere at a temperature of 450°C.

[0027]

Then, a mixed liquid in which a ratio of sulfuric acid/phosphoric acid is 1:2 is placed in a container equipped with a circulator, and the temperature is increased to 335°C. A nitride-based semiconductor thick film containing a substrate is dipped in a solution in which moisture contained in the phosphoric acid and the sulfuric acid is sufficiently evaporated at a temperature of 100°C or higher, and etching of the sapphire substrate is carried out. The sapphire substrate 11 of a thickness 300  $\mu\text{m}$  is dissolved in about 230 min. and, by continuing the etching, the substrate side of the GaN buffer layer 12, the  $\text{SiO}_2$  mask 13 and the GaN film 15 is also dissolved (Fig. 1(c)).

[0028]

Furthermore, the protective film 17 formed on the surface of the GaN film 15 is subjected to etching in a mixed liquid of nitric acid and hydrochloric acid, and the  $\text{SiO}_2$  film 16 is removed by hydrofluoric acid to form a thick film substrate by the GaN layer 15 (Fig. 1(d)). Since the protective film 17 is formed on the surface of the GaN film 15 during dissolution of the sapphire substrate, the etching causes no concavoconvex surface roughness on the surface of the GaN film 15. After the removal of the substrate, the backside of the substrate side of the nitride-based semiconductor layer may be polished to be flat.

[0029]

According to the first embodiment, since the substrate is removed by the etching solution to dissolve the substrate material as the method for removing the substrate from the nitride-based semiconductor layer formed on the sapphire substrate, compared with the removal of the sapphire substrate by polishing, the sapphire substrate can be removed without giving any damage to the nitride-based semiconductor layer. Thus, it is possible to obtain a highly crystalline nitride-based semiconductor structure by using the GaN film 15 as a thick film substrate. The sapphire substrate of a thickness 300  $\mu\text{m}$  is used. However, similar effects can be obtained in the case of a sapphire substrate of a thickness which can prevent cracks by heat distortion after a thick GaN film is formed.

[0030]

According to the first embodiment, the sapphire substrate is shown by using a C surface. However, etching can be carried out even by using a low-index surface substrate such as an M surface of (1-100) or an R surface of (1-102). Additionally, similar effects can be obtained even when a sapphire substrate slightly inclined from the C surface is used.

[0031]

The etching solution of the phosphoric acid and the sulfuric acid is set to the temperature of 335°C. However, the etching solution temperature is not limited to this temperature. As can be understood from Fig. 2, preferably, a

temperature of 300°C or higher is set when the temperature of the etching solution is changed.

[0032]

As the protective film 17 of the GaN film 35, Ti of a thickness 50 nm and Au of a thickness 0.4  $\mu\text{m}$  are used. However, the protective film is not limited to these. It is only necessary to have a thickness or use a material which can endure the mixed liquid of the phosphoric acid and the sulfuric acid during etching of the sapphire substrate. The protective film is formed on the  $\text{SiO}_2$  film in order to prevent metal contamination in the vicinity of the surface of the GaN film by the protective film 35 of Ti-Au. However, the protective film needs not be formed on the  $\text{SiO}_2$  film as long as its main purpose is to protect the GaN film 35.

[0033]

Further, titanium (Ti)-gold (Au) is used for the material of the protective film 37 of the surface of the GaN film 35. However, similar effects can be obtained in the case of materials such as platinum (Pt), Ti-Pt-Au, Ti-Pt, Au, palladium (Pd)-Au, nickel (Ni)-Au, aluminum (Al)-Au, AuZn, and AuGe, which are not etched in the mixed liquid containing phosphoric acid and sulfuric acid.

[0034]

The example in which the GaN buffer layer 32, and the GaN film 35 are formed on the sapphire substrate 31 has been described. However, the invention is not limited to this example. Similar effects can be obtained in the case of

$\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ),  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ) and  $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$  ( $0 \leq x+y \leq 1$ ), or a layer structure thereof. There is no problem even if n or p type impurities are added.

[0035]

<Second Embodiment> A second embodiment of the present invention will be described by referring to schematic views of Figs. 4(a) to 4(d). According to the second embodiment, a sapphire substrate is removed from a nitride-based semiconductor thick film grown on the sapphire substrate by an etching solution to form a nitride-based semiconductor thick film, and a nitride-based semiconductor layer is epitaxially grown by using this as a substrate to form a nitride-contained semiconductor element structure.

[0036]

According to the second embodiment, a sapphire substrate of a (0001) surface having a thickness of 300  $\mu\text{m}$  is used as a substrate material. A GaN buffer layer 32 is formed to a thickness of about 1  $\mu\text{m}$  on the sapphire substrate 31 by metalorganic chemical vapor phase epitaxy (MOVPE). Then, an  $\text{SiO}_2$  film is formed to a thickness of 0.3  $\mu\text{m}$  on the GaN buffer layer 32, and a mask 33 and an opening 34 are formed in stripe shapes in a [1-100] direction by a photolithography method and wet etching. Subsequently, vapor phase epitaxy (VPE) of a chloride transport method which uses a chloride for a III-group raw material is used, growth is carried out at a temperature of 950°C or higher, grown from the opening 34 to bury the mask 33, then the growth is

continued to grow a GaN film 35 to a thickness of 250  $\mu\text{m}$  or higher. Subsequently, a protective film is formed on the surface of the epitaxially grown layer. On the surface of the grown GaN film 35, a  $\text{SiO}_2$  film (not shown) is formed to a thickness of 50 nm, and titanium (Ti) and gold (Au) are deposited to 50 nm and 0.1  $\mu\text{m}$  respectively in thickness to form a protective film 30. After the formation of the protective film 30, and annealing is carried out at a temperature of 400°C or higher (Fig. 4(a)).

[0037]

Then, a mixed liquid of phosphoric acid and sulfuric acid is used as the etching solution, and the sapphire substrate is etched to be removed. The etching is further continued to etch the GaN film 32, the  $\text{SiO}_2$  mask 3, and the GaN film 35 in the vicinity of an interface. Subsequently, the protective film 30 of Ti-Au is removed by aqua regia (mixture of nitric acid and hydrochloric acid), and the  $\text{SiO}_2$  film 33 is removed by hydrofluoric acid (HF) to form a crystals of the GaN film 35 (Fig. 4(b)).

[0038]

Then, a nitride-based semiconductor layer structure is made on the GaN layer 35 by using metalorganic chemical vapor phase epitaxy (MOVPE). A temperature is increased to 1000°C, and the following layers are sequentially formed to make a laser element structure, i.e., an n type GaN layer 36 of a thickness 1  $\mu\text{m}$  to which Si is added, an n type  $\text{Al}_{0.15}\text{Ga}_{0.85}\text{N}$  clad layer 37 of a thickness 0.4  $\mu\text{m}$  to which Si is

added, an n type GaN optical guide layer 38 of a thickness 0.1  $\mu\text{m}$  to which Si is added, a multi-quantum well structure active layer 39 of 10 cycles which is constituted of an undoped  $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$  quantum well layer of a thickness 2.5 nm and an undoped  $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$  barrier layer of a thickness 5 nm, a p type  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$  layer 40 of a thickness 20 nm to which magnesium (Mg) is added, a p type GaN optical guide layer 41 of a thickness 0.1  $\mu\text{m}$  to which Mg is added, a p type  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$  clad layer 42 of a thickness 0.4  $\mu\text{m}$  to which Mg is added, and a p type GaN contact layer 43 of a thickness 0.5  $\mu\text{m}$  to which Mg is added. A p type electrode 44 made of palladium (Pd) of a thickness 50 nm and gold (Au) of a thickness 0.3  $\mu\text{m}$  is formed on the p type GaN contact layer 43. Lastly, an n type electrode 45 made of Ti of a thickness 50 nm and aluminum (Al) of a thickness 0.3  $\mu\text{m}$  is formed on the backside of the GaN film 35 (Fig. 4(c)).

[0039]

According to the second embodiment, by using a crystal of the GaN film 15 obtained by removing the heterosubstrate as a substrate, good crystallinity can be obtained regarding a structure of a light emitting element such as a semiconductor laser (LD) or a light emitting diode and a structure of an electronic device such as a field effect transistor. Thus, it is possible to solve the problems when the element is formed by using the heterosubstrate such as a sapphire substrate.

[0040]



According to the second embodiment, the sapphire substrate is shown by using a C surface. However, etching can be carried out even by using a low-index surface substrate such as an M surface of (1-100) or an R surface of (1-102). Additionally, similar effects can be obtained even when a sapphire substrate slightly inclined from the C surface is used.

[0041]

As the material of the protective film 37 of the GaN film 35 surface, titanium (Ti)-gold (Au) is used. However, similar effects can be obtained in the case of materials such as platinum (Pt), Ti-Pt-Au, Ti-Pt, Au, palladium (Pd)-Au, nickel (Ni)-Au, aluminum (Al)-Au, AuZn, and AuGe, which are not etched in the mixed liquid containing phosphoric acid and sulfuric acid.

[0042]

The example in which the GaN buffer layer 32, and the GaN film 35 are formed on the sapphire substrate 31 has been described. However, the invention is not limited to this example. Similar effects can be obtained in the case of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ),  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  ( $0 \leq x \leq 1$ ) and  $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$  ( $0 \leq x+y \leq 1$ ), or a layer structure thereof. There is no problem even if n or p type impurities are added.

[0043]

Further, the example in which the growth region 34 of selective growth or the  $\text{SiO}_2$  mask 33 in the vicinity of the sapphire substrate is etched in the mixed liquid has been

described. However, even the sapphire substrate may be etched by the mixed liquid, and the GaN film 32, the SiO<sub>2</sub> mask 33, and the GaN film 35 in the vicinity of the interface may be removed by polishing or the like. Additionally, after the substrate is removed, the backside of the substrate side of the nitride-based semiconductor layer may be polished to be flat.

[0044]

<Third Embodiment> A third embodiment of the present invention will be described by referring to schematic views of Figs. 5(a) to 5(d). According to the third embodiment, a nitride-based semiconductor layer, and a nitride-based semiconductor laser structure are sequentially grown on a sapphire substrate, and then the sapphire substrate is removed by an etching solution to form a nitride-based semiconductor laser element.

[0045]

First, by using a substrate in which a GaN film 32 of a thickness of about 1  $\mu\text{m}$  is formed on a (0001) surface sapphire substrate 31 of a thickness 300  $\mu\text{m}$ , an SiO<sub>2</sub> film is formed on the GaN buffer film 32, and separated into a mask 33 and a growth region 34 by a photolithography method and wet etching. The mask 33 and the growth region 34 are formed in stripe shapes of 2  $\mu\text{m}$  and 3  $\mu\text{m}$  respectively in width, and a stripe direction is a [1-100] direction. Subsequently, a GaN layer 35 of 200  $\mu\text{m}$  is formed by vapor phase epitaxy (VPE) of a chloride transport method which uses

hydrogen chloride (HCl)/gallium (Ga), ammonia ( $\text{NH}_3$ ), and hydrogen ( $\text{H}_2$ ). The GaN layer 35 is made an n type by adding Si impurities (Fig. 5(a)).

[0046]

Then, a nitride-based semiconductor layer structure is made on the GaN layer 35 by using metalorganic chemical vapor phase epitaxy (MOVPE). A temperature is increased to  $1000^\circ\text{C}$ , and the following layers are sequentially formed to make a laser element structure, i.e., an n type GaN layer 36 of a thickness  $1\text{ }\mu\text{m}$  to which Si is added, an n type  $\text{Al}_{0.15}\text{Ga}_{0.85}\text{N}$  clad layer 37 of a thickness  $0.4\text{ }\mu\text{m}$  to which Si is added, an n type GaN optical guide layer 38 of a thickness  $0.1\text{ }\mu\text{m}$  to which Si is added, a multi-quantum well structure active layer 39 of 10 cycles which is constituted of an undoped  $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$  quantum well layer of a thickness  $2.5\text{ nm}$  and an undoped  $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$  barrier layer of a thickness  $5\text{ nm}$ , a p type  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$  layer 40 of a thickness  $20\text{ nm}$  to which magnesium (Mg) is added, a p type GaN optical guide layer 41 of a thickness  $0.1\text{ }\mu\text{m}$  to which Mg is added, a p type  $\text{Al}_{0.1}\text{Ga}_{0.9}\text{N}$  clad layer 42 of a thickness  $0.4\text{ }\mu\text{m}$  to which Mg is added, and a p type GaN contact layer 43 of a thickness  $0.5\text{ }\mu\text{m}$  to which Mg is added. A p type electrode 44 made of palladium (Pd) of a thickness  $50\text{ nm}$  and gold (Au) of a thickness  $0.3\text{ }\mu\text{m}$  is formed on the p type GaN contact layer 43. Further, after the p type electrode 44 is formed, heat treatment is carried out at a temperature of  $450^\circ\text{C}$ . This p type electrode 44 also serves to protect the surfaced of the

GaN film 43 during etching of the sapphire substrate 21 (Fig. 5(b)).

[0047]

Then, the nitride-based semiconductor laser structure obtained in Fig. 5(b) is dipped in the etching solution in which a ratio of sulfuric acid/phosphoric acid is set to 1:2, and a temperature is set to 350°C, and the sapphire substrate is removed. As shown in Fig. 3, since etching can be carried out at a rate of 150  $\mu\text{m}/\text{hour}$  at the temperature of 350°C, it is possible to remove the sapphire substrate of a thickness 300  $\mu\text{m}$  within about 120 min. Further, by etching, the GaN film 32, the mask 33 and even a part of the GaN film 35 are dissolved. The GaN film 35 is etched to about 50  $\mu\text{m}$  in the vicinity of the interface with the GaN buffer layer 32. Lastly, an n electrode 45 made of Ti of a thickness 50 nm and aluminum (Al) of a thickness 0.3  $\mu\text{m}$  is formed on the backside of the exposed GaN film 35 (Fig. 5(c)).

[0048]

In the nitride-based semiconductor laser element manufactured according to each of the second and third embodiments, since cleavage is possible on an M surface which is a cleavage direction of the GaN film 35 by using the GaN thick film as a substrate, a complex step such as reactive ion etching is unnecessary, and a highly smooth nitride-based semiconductor laser element can be manufactured. Moreover, since the n type electrode 45 can be formed on the backside

of the GaN film 35, the conventional reactive ion etching step is made unnecessary as the electrode forming step, and thus the process can be simplified.

[0049]

According to the third embodiment, the sapphire substrate is shown by using a C surface. However, etching can be carried out even by using a low-index surface substrate such as an M surface of (1-100) or an R surface of (1-102). Additionally, similar effects can be obtained even when a sapphire substrate slightly inclined from the C surface is used.

[0050]

By the etching solution containing the mixed liquid of the phosphoric acid and the sulfuric acid, the sapphire substrate 31, the GaN film 32, the mask 33, and even the GaN film 35 in the vicinity of the interface with the GaN buffer layer 32 up to about 50  $\mu\text{m}$  are dissolved to be removed. However, the invention is not limited to this. After the removal of the sapphire substrate by the etching solution, the GaN film 32 and the mask 33 may be removed by polishing, the GaN film 35 in the vicinity of the interface with the GaN buffer layer 32 may be removed, and then an n type electrode, and a resonator mirror surface by cleavage may be formed.

[0051]

[Effects of the Invention]

According to the present invention, since the substrate is removed by using the solution to dissolve the

substrate material of the nitride-based semiconductor, it is possible to remove the substrate without giving any influence such as cracks to the nitride-based semiconductor grown layer on the substrate.

[Brief Description of Drawings]

[Fig. 1]

Process views showing a method for manufacturing a nitride-based semiconductor thick layer according to a first embodiment of the present invention.

[Fig. 2]

A view showing a change in etching rate of sapphire when a ratio of sulfuric acid/phosphoric acid in a mixed liquid is changed.

[Fig. 3]

A view showing changes in etching rates of sapphire and GaN with respect to a change in temperature of the mixed liquid of the phosphoric acid and the sulfuric acid.

[Fig. 4]

Process views showing a method for manufacturing a nitride-based semiconductor element according to a second embodiment of the present invention.

[Fig. 5]

Process views showing a method for manufacturing a nitride-based semiconductor element according to a third embodiment of the present invention.

[Fig. 6]

A schematic sectional view showing a structure of a

conventional nitride-based compound semiconductor laser.

[Description of Reference Numerals]

- 11 Sapphire substrate
- 12 GaN buffer film
- 13 Mask
- 14 Growth region
- 15 GaN film
- 16 SiO<sub>2</sub> film
- 17 Protective film made of titanium (Ti)-gold (Au)
- 31 Sapphire substrate of C surface
- 32 GaN buffer film
- 33 Mask
- 34 Growth region
- 35 GaN film to which n type impurities are added
- 36 n type GaN layer
- 37 n type Al<sub>0.15</sub>Ga<sub>0.85</sub>N clad layer
- 38 n type GaN optical guide layer
- 39 Multi-quantum well structure active layer of 10 cycles  
which is made of undoped In<sub>0.2</sub>Ga<sub>0.8</sub>N and undoped In<sub>0.05</sub>Ga<sub>0.95</sub>N  
barrier layer
- 40 p type Al<sub>0.2</sub>Ga<sub>0.8</sub>N layer of thickness 20 nm
- 41 p type GaN optical guide layer
- 42 p type Al<sub>0.1</sub>Ga<sub>0.9</sub>N clad layer
- 43 p type contact layer
- 44 p type electrode made of palladium (Pd) and gold (Au)
- 45 n electrode made of titanium (Ti) and aluminum

[Name of Document] Abstract

[Abstract]

[Problem]

To suppress an influence on a nitride-based semiconductor grown layer when a substrate is removed from the nitride-based semiconductor layer epitaxially grown on a heterosubstrate.

[Solving Means]

A flat-surface highly crystalline GaN film 15 is grown to a thickness of 250  $\mu\text{m}$  on a sapphire substrate 11 of a (0001) surface by vapor phase growth of a chloride transport method. Then, the substrate 11 is dissolved to be removed from the GaN thick film 15 grown on the sapphire substrate 11 by using an etching solution to dissolve a sapphire substrate material.

[Selected Drawing] Fig. 1



Name of Document: Drawing

Fig. 1

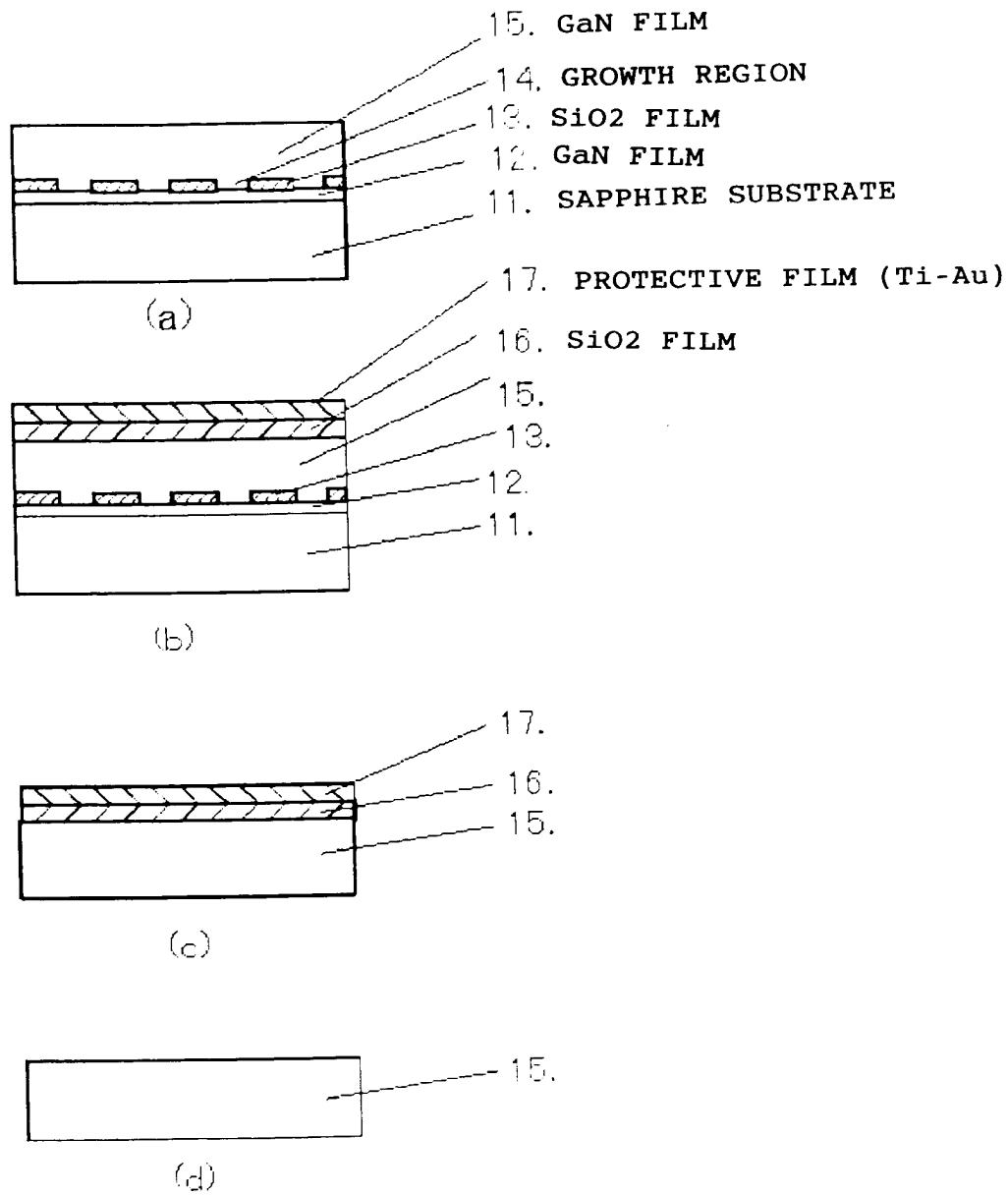


Fig. 2

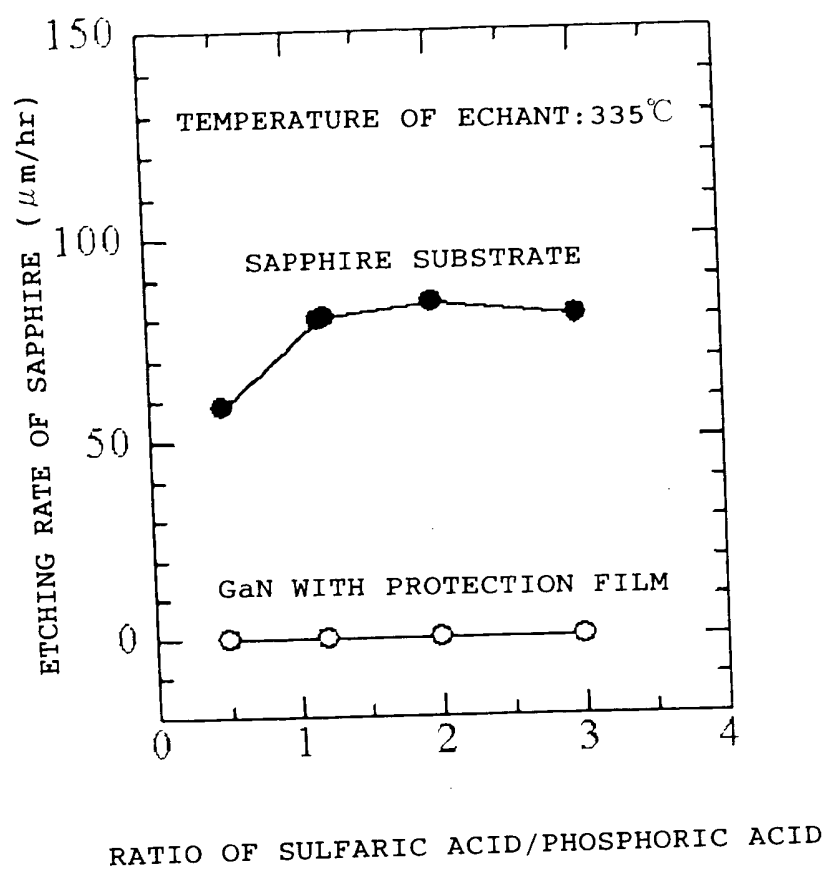


Fig. 3

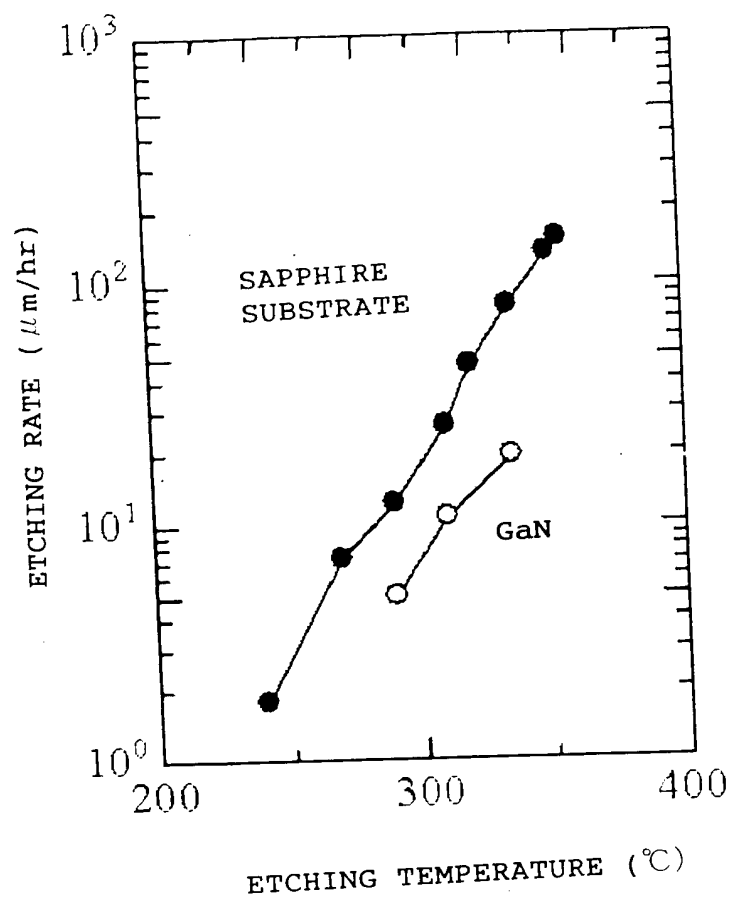
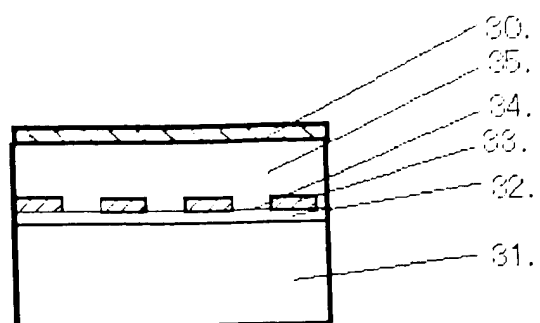


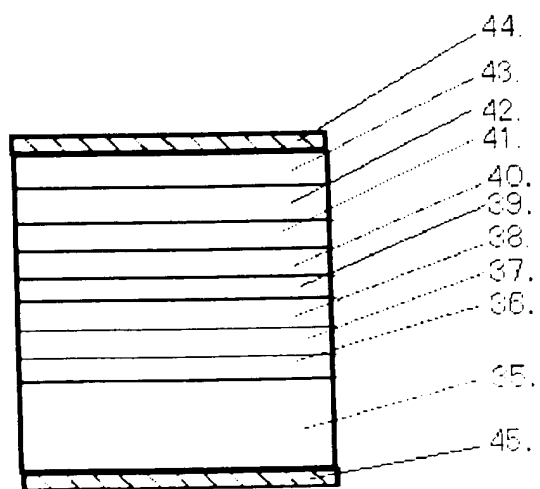
Fig. 4



(a)

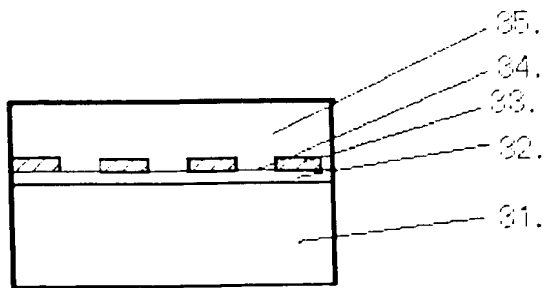


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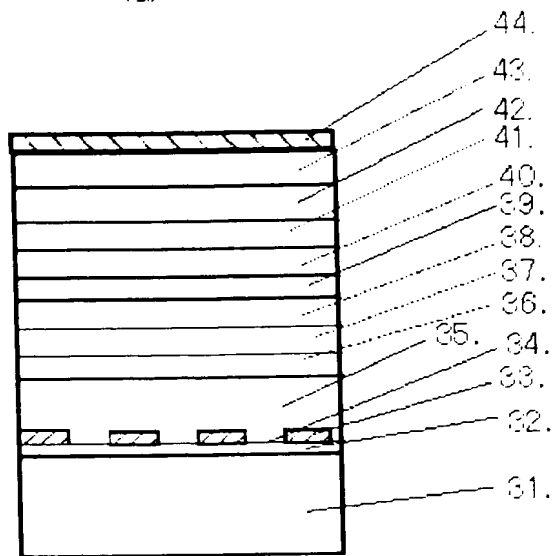


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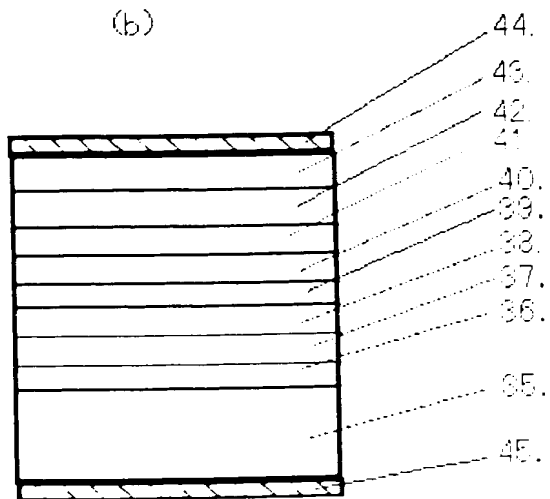
Fig. 5



(a)



(b)



(c)

Fig. 6

